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DECLARATION

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AND I MAKE THIS SOLEMN DECLARATION conscientiously believing the same to be true and correct.

  
Yuumi Amakawa

JAPAN PATENT OFFICE

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[Title of the Invention] Plastic Packing Body

[Claims]

[Claim 1] A plastic packing body having an islands-in-the-sea structure constituted by a sea portion of a polyester resin and island portions of an oxygen absorbing gas barrier resin composition containing an oxidizing organic component and a transition metal catalyst, wherein no oxidizing organic component is present in the sea portion.

[Claim 2] A plastic packing body according to claim 1, wherein the island portions have an average domain diameter  $r$  of smaller than  $3.5 \mu\text{m}$  and a dispersion parameter  $Q$  of more than 0.68, which are represented by the following formulas (1) and (2),

$$r = \frac{\sum_{i=1}^n r_i}{n} \quad \text{--- (1)}$$

$$Q = \frac{\sum_{i=1}^n Q_i \cdot \ln Q_i}{\ln(1/n)} \quad \text{--- (2)}$$

wherein  $r_i$  is a domain diameter,  $n$  is a number of domains, the domain diameter  $r_i$  being  $r_i = (a_i + b_i)/2$  wherein  $a_i$  is a short diameter of the domain and  $b_i$  is a long diameter of the domain, and

$$Q_i = \frac{\pi (r_i/2)^2}{\sum_{i=1}^n \pi (r_i/2)^2}$$

[Claim 3] A plastic packing body according to claim 1 or 2, wherein the oxygen absorbing gas barrier resin composition is not more than 70% by weight.

[Claim 4] A plastic packing body according to any one of claims 1 to 3, wherein the oxygen absorbing gas barrier resin composition contains a polyamide resin having a terminal amino group concentration of not less than  $40 \text{ eq}/10^6 \text{ g}$ .

[Claim 5] A plastic packing body according to any one of

claims 1 to 4, wherein the oxygen absorbing gas barrier resin composition contains an oxidizing organic component of not more than 10% by weight based on the resin composition.

[Claim 6] A plastic packing body according to any one of claims 1 to 5, wherein the oxidizing organic component is a polymer derived from polyenes.

[Claim 7] A plastic packing body according to claim 6, wherein the oxidizing organic component is an acid-modified polyene polymer.

[Claim 8] A plastic packing body according to any one of claims 1 to 7, wherein the transition metal catalyst is a carboxylate of cobalt.

[Claim 9] A plastic packing body according to any one of claims 1 to 8, wherein the oxygen absorbing gas barrier resin composition contains a transition metal catalyst in an amount of 1 to 3000 ppm calculated as a metal.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

This invention relates to a plastic packing body having gas barrier property and, more specifically, to a plastic packing body having excellent oxygen absorbing gas barrier property as well as excellent transparency.

[0002]

[Prior Art]

Metal cans, glass bottles and various kinds of plastic containers have heretofore been used as packing containers. Among them, the plastic containers have such advantages as being light in weight and excellent in shock resistance accompanied, however, by such problems as degeneration of the contents and loss of flavor due to oxygen that permeates through the container walls.

[0003]

In particular, the metal cans and glass bottles permit no oxygen to permeate through the container walls and, therefore, the only oxygen remaining in the containers becomes a problem. The plastic containers, however, permit oxygen to permeate through the container

walls to a degree that is not negligible arousing a problem from the standpoint of preserving the contents.

[0004]

In order to prevent this, there has been proposed a plastic multi-layer container of a laminated structure comprising an intermediate layer of a resin composition obtained by blending a gas barrier thermoplastic resin having an oxygen permeation coefficient at 20°C and 0%RH of not more than  $10^{-12}$  cc·cm/cm<sup>2</sup>·sec·cmHg and a water adsorbing amount at 20°C and 100%RH of not less than 0.5% with an organometal complex of a transition metal, and providing moisture-resistant thermoplastic resin layers on both sides of the intermediate layer (patent document 1).

[0005]

There has further been proposed a barrier wall for packing comprising a polymer including a composition having oxygen-trapping property or including a layer of the above composition, the composition trapping oxygen as the oxidizing organic component is oxidized with a metal catalyst, the oxidizing organic component being a polyamide and, particularly, a xylylene group-containing polyamide (patent document 2).

[0006]

The oxygen absorbing resin composition containing the above transition metal catalyst has an advantage in that it is substantially transparent, can be applied to packing containers that require transparency and, besides, the polyamide resin by itself is a resin having excellent oxygen barrier property. The polyamide resin, however, is deteriorated by oxidation and permits oxygen to permeate through the container walls with the passage of time.

In order to solve the above problem, the present applicant has attempted to blend the polyamide resin with an oxidizing organic component and a transition metal catalyst to maintain low the permeation of oxygen through the resin composition for extended periods of time, and has proposed a resin composition having oxygen absorbing gas barrier property (patent document 3).

[0007]

[Patent document 1] Japanese Unexamined Patent Publication (Kokai) No. 1-278344

[Patent document 2] Japanese Patent No. 2991437

[Patent document 3] Japanese Unexamined Patent Publication (Kokai) No. 2002-241608

[0008]

[Problems that the Invention is to Solve]

The packing container using the above resin composition as the intermediate layer exhibits excellent oxygen absorbing gas barrier property for extended periods of time but absorbs oxygen after it has arrived at the intermediate layer permeating through the inner and outer layers requiring a predetermined period of time until oxygen absorbing property is exhibited. Therefore, the initial oxygen absorbing property is inferior to that of a packing container of a single layer.

As will be described later, further, though the above resin composition exhibits excellent transparency, it was confirmed that a packing container of a blend of the above resin composition and a thermoplastic resin such as polyester resin possesses decreased transparency depending upon the manner of blending.

[0009]

It is, therefore, an object of the present invention to provide a plastic packing body of a single layer capable of efficiently exhibiting such functions as gas barrier property and having excellent transparency and, particularly, initial oxygen absorbing barrier property.

[0010]

[Means for Solving the Problems]

According to the present invention, there is provided a plastic packing body having an islands-in-the-sea structure constituted by a sea portion of a polyester resin and island portions of an oxygen absorbing gas barrier resin composition containing an oxidizing organic component and a transition metal catalyst, wherein no oxidizing organic component is present in the sea portion.

[0011]

In the present invention, it is desired that:



1. The island portions has an average domain diameter  $r$  of less than  $3.5 \mu\text{m}$  and a dispersion parameter  $Q$  of more than 0.68, which are represented by the following formulas (1) and (2),

$$r = \frac{\sum_{i=1}^n r_i}{n} \quad \text{--- (1)}$$

$$Q = \frac{\sum_{i=1}^n Q_i \cdot \ln Q_i}{\ln(1/n)} \quad \text{--- (2)}$$

wherein  $r_i$  is a domain diameter,  $n$  is a number of domains, the domain diameter  $r_i$  being  $r_i = (a_i + b_i)/2$  wherein  $a_i$  is a short diameter of the domain and  $b_i$  is a long diameter of the domain, and

$$Q_i = \frac{\pi (r_i/2)^2}{\sum_{i=1}^n \pi (r_i/2)^2};$$

2. The oxygen absorbing gas barrier resin composition is not more than 70% by weight;
  3. The oxygen absorbing gas barrier resin composition contains a polyamide resin having a terminal amino group concentration of not less than  $40 \text{ eq}/10^6 \text{ g}$ ;
  4. The oxygen absorbing gas barrier resin composition contains an oxidizing organic component of not more than 10% by weight based on the resin composition;
  5. The oxidizing organic component is a polymer derived from polyenes and, particularly, is an acid-modified polyene polymer;
  6. The transition metal catalyst is a carboxylate of cobalt and
  7. The oxygen absorbing gas barrier resin composition contains a transition metal catalyst in an amount of 1 to 3000 ppm calculated as a metal.
- [0012]

In the present invention, an important feature resides in the possession of an islands-in-the-sea structure constituted by a sea portion of a polyester

resin and island portions of an oxygen absorbing gas barrier resin composition containing an oxidizing organic component and a transition metal catalyst, wherein no oxidizing organic component is present in the sea portion. This makes it possible to provide a plastic packing body exhibiting excellent oxygen absorbing gas barrier property and having excellent transparency.

The plastic packing body of the invention has the so-called islands-in-the-sea structure in which dispersed phases (island portions) of the oxygen absorbing gas barrier resin composition are present in a continuous phase (sea portion) of the polyester resin. Here, as will be described later, it was learned that the transparency decreases if the oxidizing organic component in the oxygen absorbing gas barrier resin composition is present not only in the dispersed phases but also in the continuous phase of the polyester resin.

[0013]

Fig. 1 is a view schematically illustrating an electron microphotograph of an injected sheet molded by dry-blending an oxygen absorbing gas barrier resin composition obtained by biaxially kneading a polyamide resin, an oxidizing organic component and a transition metal catalyst together, and a polyester resin at a weight ratio of 50:50, and Fig. 2 is a view schematically illustrating an electron microphotograph of an injected sheet molded from a blend that is obtained by biaxially kneading together the four components of a polyester resin, a polyamide resin constituting an oxygen absorbing gas barrier resin composition, an oxidizing organic component and a transition metal catalyst.

It will be learned from Fig. 1 and Fig. 2 that there have been formed islands-in-the-sea structures in which the island portions (b) of the oxygen absorbing gas barrier resin composition are present in the sea portion (a) of the polyester resin. In Fig. 1, the oxidizing component (c) is present only in the dispersed phase of the polyamide resin while in Fig. 2, the oxidizing organic component is present not only in the dispersed phases but

also in the polyester resin of the continuous phase.  
[0014]

Fig. 3 is a diagram illustrating hazes of sheets obtained by stretching the injected sheets shown in Fig. 1 and Fig. 2 into 3 times x 3 times in the longitudinal and transverse directions. As will be obvious from Fig. 3, the sheet (Fig. 1) in which the oxidizing organic component is present in the island portions only has a haze of about 12% and features excellent transparency. On the other hand, the sheet shown in Fig. 2 in which the oxidizing organic component is present not only in the island portions but also in the sea portion has a haze more than 60% and, therefore, has a very poor transparency. The haze increases as described above depending upon the state of the oxidizing organic component because of the fact that the scattering points of light increase if the oxidizing organic component used in the invention is present not only in the island portions but also in the sea portion. Besides, since the oxidizing organic component is not favorably compatible with the polyester resin forming the sea portion, the oxidizing organic component present in the sea portion having grain sizes that trigger the scattering of light also serves as a factor for increasing the haze.

Here, in the invention, the fact that no oxidizing organic component is present in the sea portion desirably stands for that quite no oxidizing organic component is present therein but, not limited thereto only, also encompasses a meaning that its presence is as close to zero as possible.

[0015]

In the present invention, further, the island portions comprising the oxygen absorbing gas barrier resin composition has an average domain diameter represented by the above formula (1) of less than  $3.5 \mu\text{m}$  and a dispersion parameter  $Q$  represented by the above formula (2) of more than 0.68. That is, the island portions comprising the oxygen absorbing gas barrier resin composition are present having relatively small particle

sizes and in a narrow particle size profile in the sea portion, making it possible to fully exhibit such functions as gas barrier property compounded by the state of the above-mentioned oxidizing organic component, as well as to feature excellent transparency. If the dispersion parameter  $Q$  is 1, the island portions have a monotonously dispersed domain diameter, i.e., the island sizes become uniform as  $Q$  approaches 1.

[0016]

Fig. 4 is a diagram illustrating a relationship between the dispersion parameter  $Q$  represented by the above formula (2) of a preform having the islands-in-the-sea structure comprising the polyester resin and the oxygen absorbing barrier resin composition and the haze (%) of the sheet cut out from the shoulder portion of a bottle obtained by biaxially stretch-blow-molding the above preform. As will be obvious from Fig. 4, the haze decreases as the dispersion parameter  $Q$  representing the particle size profile of the island portions approaches 1, and the transparency is improved. In the case of the packing body that requires the transparency and, particularly, the bottle, in general, it is desired that the haze is not more than 20%. With the packing body of the invention, the haze becomes less than 20% when the dispersion parameter  $Q$  is near 0.68, and satisfactory transparency is maintained.

Further, upon controlling not only the dispersion parameter  $Q$  but also the average domain diameter of the island portions to be less than  $3.5\ \mu\text{m}$  and, particularly, not more than  $3\ \mu\text{m}$  as will be described later, it is made possible to fulfill all of the functions such as oxygen absorbing gas barrier property, transparency, mechanical strength, etc.

[0017]

[Embodiments of the Invention]

The packing body of the invention has oxygen absorbing property and gas barrier property and, further, has the islands-in-the-sea structure in which the sea portion (i.e., matrix) is formed by the polyester resin

and the island portions are formed by the oxygen absorbing gas barrier resin composition containing the oxidizing organic component and the transition metal catalyst.

[0018]

(Polyester resins)

It is desired that the polyester resin that forms the matrix of the packing body of the invention can be biaxially stretch-blow-molded and crystallized, and there can be used thermoplastic polyesters such as polyethylene terephthalate, polybutylene terephthalate and polyethylene naphthalate, or a blend of these polyesters with a polycarbonate or an arylate resin. In the present invention, it is desired to use a polyethylene terephthalate (PET) type polyester in which most (usually, not less than 80 mol%) of the ester recurring units are ethylene terephthalate units, and having a glass transition point ( $T_g$ ) of 50 to 90°C and, particularly, 55 to 80°C and a melting point ( $T_m$ ) of 200 to 275°C and, particularly, 220 to 270°C.

[0019]

As the PET type polyester, a homopolyethylene terephthalate is most desired. However, a copolymerized polyester having an ethylene terephthalate unit content lying in the above range, too, can be preferably used.

In the copolymerized polyester, examples of the dibasic acid other than the terephthalic acid include aromatic dicarboxylic acids such as isophthalic acid, phthalic acid and naphthalenedicarboxylic acid; alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid; aliphatic dicarboxylic acids such as succinic acid, adipic acid, sebacic acid and dodecanedioic acid, which can be used in one kind or in two or more kinds in combination. As the diol component other than the ethylene glycol, there can be exemplified propylene glycol, 1,4-butanediol, diethylene glycol, 1,6-hexylene glycol, cyclohexane dimethanol and ethylene oxide adduct of bisphenol A, which can be used in one kind or in two or more kinds.

[0020]

The resin that constitutes the continuous phase

should have a molecular weight at least large enough for forming a film. When the resin is, for example, the above-mentioned polyester, it is desired that its intrinsic viscosity (I.V) is in a range of 0.6 to 1.40 dl/g and, particularly, 0.63 to 1.30 dl/g.

[0021]

(Oxygen absorbing gas barrier resin compositions)

In the packing body of the invention, the oxygen absorbing gas barrier resin composition present as the dispersed phase in the polyester resin which is the continuous phase, is, concretely, a resin composition comprising an oxidizing organic component, a transition metal catalyst and a gas barrier resin.

That is, upon oxidizing the oxidizing organic component, it is made possible to absorb and trap oxygen, to enhance oxygen barrier function of the gas barrier resin and to express oxygen absorbing property without deteriorating the gas barrier property that results from the deterioration of the gas barrier resin by oxidation. Further, the transition metal catalyst is blended for accelerating the oxidation of the oxidizing organic component. The oxidizing organic component and the transition metal catalyst, too, are dispersed like islands together with the gas barrier resin.

[0022]

[Gas barrier resins]

As the gas barrier resin that can be most favorably used for the gas barrier resin composition of the present invention, there can be exemplified polyamide resins such as nylon 6, nylon 6·6, nylon 6/6·6 copolymer, polymetaxylenediadipamide (MXD 6), nylon 6·10, nylon 11, nylon 12 and nylon 13.

Among these polyamides, it is desired to use a polyamide resin having terminal amino groups in an amount of not less than  $40 \text{ eq}/10^6 \text{ g}$  and, particularly, more than  $50 \text{ eq}/10^6 \text{ g}$  from the standpoint of suppressing the deterioration of the polyamide resin by oxidation.

It is, further, desired to use those having amide groups in a number in a range of 5 to 50 and,

particularly, 6 to 20 per 100 carbon atoms. These polyamides, too, should have molecular weights large enough for forming a film and should desirably have a relative viscosity of, for example, not less than 1.1 and, particularly, not less than 1.5 as measured in the concentrated sulfuric acid (concentration of 1.0 g/dl) at 30°C.

[0023]

As the gas barrier resin other than the polyamide resin, there can be exemplified an ethylene/vinyl alcohol copolymer and, desirably, a saponified product of a copolymer obtained by so saponifying an ethylene/vinyl acetate copolymer having an ethylene content of 20 to 60 mol% and, particularly, 25 to 50 mol% that the degree of saponification is not less than 96% and, particularly, not less than 99 mol%. The ethylene/vinyl alcohol copolymer (saponified product of ethylene/vinyl acetate copolymer) should have a molecular weight large enough for forming a film and, generally, should desirably have an intrinsic viscosity of not less than 0.01 dl/g and, particularly, not less than 0.05 dl/g in a mixed solvent of phenol/water at a weight ratio of 85/15 at 30°C.

[0024]

[Oxidizing organic components]

As the oxidizing organic component to be added to the gas barrier resin, there can be exemplified an ethylenically unsaturated group-containing polymer. Namely, the polymer has a carbon-to-carbon double bond; i.e., the double-bonded portion is easily oxidized with oxygen to thereby absorb and trap oxygen.

[0025]

The ethylenically unsaturated group-containing polymer is derived by, for example, using a polyene as a monomer. Though not limited thereto only, preferred examples of the polyene include conjugated dienes such as butadiene and isoprene; chained nonconjugated dienes such as 1,4-hexadiene, 3-methyl-1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 4,5-dimethyl-1,4-hexadiene, and 7-methyl-1,6-octadiene; cyclic

nonconjugated dienes such as methyltetrahydroindene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-isopropylidene-2-norbornene, 5-vinylidene-2-norbornene, 6-chloromethyl-5-isopropenyl-2-norbornene and dicyclopentadiene; trienes such as 2,3-diisopropylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene, and 2-propenyl-2,2-norbornadiene; and chloroprene.

[0026]

Namely, as an oxidizing organic component, there can be used a homopolymer of the above polyene, a random copolymer of a combination of two or more kinds of the above polyenes or of a combination thereof with other monomers, or a block copolymer. As the other monomers to be copolymerized with the above polyene, there can be exemplified an  $\alpha$ -olefin having 2 to 20 carbon atoms, such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-nonadecene, 1-eicocene, 9-methyl-1-decene, 11-methyl-1-dodecene and 12-ethyl-1-tetradecene. There can be further used styrene, vinyltriene, acrylonitrile, methacrylonitrile, vinyl acetate, methyl methacrylate and ethyl acrylate.

[0027]

Among the polymers derived from the above-mentioned polyenes, there can be preferably used polybutadiene (BR), polyisoprene (IR), natural rubber, nitrile-butadiene rubber (NBR), styrene-butadiene rubber (SBR), chloroprene rubber, and ethylene-propylene-diene rubber (EPDM) to which only, however, the invention is in no way limited.

[0028]

It is desired that to these polyene type polymers has been introduced a carboxylic acid group, carboxylic anhydride group or hydroxyl group. As the monomer used for introducing these functional groups, there can be used an ethylenically unsaturated monomer having the above functional group.

As the monomer, it is desired to use an unsaturated carboxylic acid or derivatives thereof. Concrete examples



include  $\alpha, \beta$ -unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid and tetrahydrophthalic acid; unsaturated carboxylic acid such as bicyclo[2,2,1]hepto-2-5,6-dicarboxylic acid;  $\alpha, \beta$ -unsaturated carboxylic anhydrides such as maleic anhydride, itaconic anhydride, citraconic anhydride and tetrahydrophthalic anhydride; and unsaturated carboxylic anhydrides such as bicyclo[2,2,1]hepto-2-ene-5,6-dicarboxylic anhydride and the like.

[0029]

The acid-modified polyene type polymer can be produced by using a resin having a carbon-to-carbon double bond as a base polymer, and graft-copolymerizing the base polymer with an unsaturated carboxylic acid or with a derivative thereof by a known means, or by the random copolymerization of the above polyene with an unsaturated carboxylic acid or a derivative thereof.

It is desired that the acid-modified polyene polymer particularly suited for the invention contains the unsaturated carboxylic acid or the derivative thereof in an amount of 0.01 to 10 % by weight. When the content of the unsaturated carboxylic acid or the derivative thereof lies within the above range, the acid-modified polyene polymer favorably disperses in the polyamide resin to smoothly absorb oxygen.

[0030]

In addition to the above ethylenically unsaturated group-containing polymer, there can be used, as an oxidizing organic component, a polymer that can be easily oxidized by itself, such as polypropylene or ethylene/propylene copolymer.

[0031]

In the present invention, it is desired that the above oxidizing organic copolymer has a viscosity in a range of 1 to 200 Pa·s at 40°C from the standpoint of moldability and the like.

It is further desired that the oxidizing organic component is used in an amount of not more than 10% by

weight per the resin composition.

[0032]

[Transition metal catalysts]

As the transition metal catalyst used together with the above-mentioned oxidizing organic component, there can be preferably used metals of the Group VIII of periodic table, such as iron, cobalt and nickel. There can be, further, used metals of the Group I, such as copper and silver; metals of the Group IV such as tin, titanium and zirconium, metals of the Group V such as vanadium; metals of the Group VI such as chromium; and metals of the Group VII such as manganese, etc. Among them, cobalt is particularly suited for the object of the invention since it promotes oxygen absorbing property (oxidation of the oxidizing organic component) to a striking degree.

[0033]

The transition metal catalyst is, usually, used in the form of an inorganic salt, an organic salt or a complex of the above transition metal having a low valency.

As the inorganic salt, there can be used a halide such as a chloride, an oxy salt of sulfur, such as a sulfate, an oxy acid salt of nitrogen, such as a nitrate, a phosphorus oxy salt of a phosphate, and a silicate.

As the organic salt, there can be exemplified a carboxylate, a sulfonate and a phosphate. For the object of the invention, however, a carboxylate is preferred. Concrete examples thereof include transition metal salts such as of acetic acid, propionic acid, isopropionic acid, butanoic acid, isobutanoic acid, pantanoic acid, hexanoic acid, heptanoic acid, isoheptanoic acid, octanoic acid, 2-ethylhexanoic acid, nonanoic acid, 3,5,5-trimethylhexanoic acid, decanoic acid, neodecanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, margaric acid, stearic acid, arachic acid, linderic acid, tsuzuic acid, petroselinic acid, oleic acid, linolic acid, linoleic acid, arachidonic acid, formic acid, oxalic acid, sulfamic acid, and naphthenic acid.

[0034]

As the complex of a transition metal, there can be exemplified a complex with  $\beta$ -diketone or with  $\beta$ -keto acid ester. As the  $\beta$ -diketone or  $\beta$ -keto acid ester, there can be used, for example, acetylacetone, ethyl acetoacetate, 1,3-cyclohexadion, methylene bis-1,3-cyclohexadion, 2-benzyl-1,3-cyclohexadion, acetyl tetralone, palmitoyl tetralone, stearoyl tetralone, benzoyl tetralone, 2-acetylcyclohexanone, 2-benzoylcyclohexanone, 2-acetyl-1,3-cyclohexadion, benzoyl-p-chlorobenzoylmethane, bis(4-methylbenzoyl)methane, bis(2-hydroxybenzoyl)methane, benzoylacetone, tribenzoylmethane, diacetylbenzoylmethane, stearoylbenzoylmethane, palmitoylbenzoylmethane, lauroylbenzoylmethane, dibenzoylmethane, bis(4-chlorobenzoyl)methane, benzoylacetylphenylmethane, stearoyl(4-methoxybenzoyl)methane, butanoylacetone, distearoylmethane, stearoylacetone, bis(cyclohexanoyl)methane and dipivaloylmethane.

[0035]

In the present invention, further, it is desired that the transition metal catalyst is added in an amount of 1 to 3000 ppm and, particularly, 50 to 2000 ppm calculated as a metal based on the resin composition.

[0036]

[Islands-in-the-sea structure]

The present invention has the islands-in-the-sea structure in which the oxygen absorbing gas barrier resin composition is present as a dispersed phase in a continuous phase of the polyester resin, the oxidizing organic component without being present in the sea portion of the polyester resin.

It is desired that the island portions formed by the oxygen absorbing gas barrier resin composition are so controlled for their particle diameter that the average domain diameter represented by the following formula (1),

$$r = \frac{\sum_{i=1}^n r_i}{n} \quad \text{--- (1)}$$

wherein  $r_i$  is a domain diameter,  $n$  is a number of

domains, the domain diameter  $r_i$  being  $r_i = (a_i + b_i)/2$  wherein  $a_i$  is a short diameter of the domain and  $b_i$  is a long diameter of the domain, is less than  $3.5 \mu\text{m}$  and, particularly, not more than  $3.0 \mu\text{m}$  from such a standpoint that the oxygen absorbing gas barrier resin composition exhibits its properties to a sufficiently degree yet maintaining transparency. Too large particle diameters of the island portions may cause a decrease in the functions such as gas barrier property, transparency and mechanical strength.

Further, the oxygen absorbing gas barrier resin composition has a high affinity to water and, therefore, tends to absorb water from the atmosphere and the content to which it is in contact. Due to the absorbed water, the resin composition itself is whitened at the time of heating prior to the molding deteriorating the moldability. Therefore, if the oxygen absorbing gas barrier resin is sealed in the polyester resin as in the present invention, then the moldability is effectively avoided from being deteriorated by water, and favorably molded articles can be obtained.

[0037]

To form the islands-in-the-sea structure, it is desired, as described above, to prepare the oxygen absorbing gas barrier resin composition in advance and blends it with the polyester resin. Namely, the gas barrier resin, oxidizing organic component and transition metal catalyst are extruded through a biaxial extruder while effecting the de-aeration to prepare a stranded resin composition which is, thereafter, pelletized and is fed to a hopper of an extruder while being dry-blended with the polyester resin.

[0038]

The phase structure of the two-component blend of the polyester resin and the oxygen absorbing gas barrier resin composition varies depending upon the molding conditions such as melt viscosity, composition, shape of the screw, revolving speed, temperature and method of blending. Among them, what are particularly important are

the melt viscosity, composition and method of blending.  
[0039]

In the above islands-dispersed-in-the-sea structure, when it is desired to increase the concentration of the island portions, the polyester resin and the oxygen absorbing gas barrier resin composition are so combined together that the oxygen absorbing gas barrier resin composition has a melt viscosity relatively higher than that of the polyester resin, and the ratio of mixing the oxygen absorbing gas barrier resin composition is increased. That is, the polyester resin and the gas barrier resin composition are melt-mixed together in an extruder. In this case, the resin having a higher melt viscosity tends to form island portions and the resin having a lower melt viscosity tends to form the sea portion.

However, if a difference is too great between the melt viscosity of the oxygen absorbing gas barrier resin composition and the melt viscosity of the polyester resin, the average domain diameter of the island portions becomes great or the dispersion parameter  $Q$  becomes small despite the resins are mixed under the above conditions, and a favorable resin composition is not obtained. In such a case, in order to suppress the average domain diameter of the island portions to be less than  $3.5\ \mu\text{m}$  and to maintain the dispersion parameter  $Q$  to be not less than 0.68, the oxygen absorbing gas barrier resin composition and the polyester resin are once melted and kneaded in the biaxial extruder, pelletized and, thereafter, are molded. This is because, upon melting and kneading the two together prior to the molding, the resins are further kneaded forming a resin composition satisfying both the dispersion parameter  $Q$  and the average domain diameter.  
[0040]

When it is desired to increase the concentration of the matrix resin phase, on the other hand, the concentration of the oxygen absorbing gas barrier resin composition which is the island component may be decreased. In melting and mixing the resins as described

above, in general, the component of a larger amount tends to form the sea portion and the component of a smaller amount tends to form the island portions.

To achieve the desired islands-in-the-sea structure, therefore, it becomes necessary to bring into consideration the melt viscosity, composition and method of blending the resins in combination. In the present invention, however, it is desired to use the polyester resin that forms the sea portion in an amount of not less than 30% by weight for forming the above-mentioned islands-in-the-sea structure. To suppress the average domain diameter of the island portions to be less than 3.5  $\mu\text{m}$ , further, it is desired to use the oxygen absorbing gas barrier resin composition in an amount of not more than 70% by weight. In order to attain the oxygen absorbing performance to a sufficient degree, however, it is desired to use the oxygen absorbing gas barrier resin composition in an amount of not less than 20% by weight. [0041]

The particle diameter can be controlled by adjusting the mixing conditions such as the mixing ratio of the polyester resin and the oxygen absorbing gas barrier resin composition, composition such as the amount of blending the oxidizing organic component in the oxygen absorbing gas barrier resin composition, melt viscosity at the time of effecting the melting and mixing, mixing time, shearing rate and melting temperature.

For example, the mixing ratio of the polyester resin (A) and the oxygen absorbing gas barrier resin composition (B) is desirably in a range of A:B = 30:70 to 80:20 on the basis of weight as described above. When a polyene type polymer such as a maleic anhydride-modified polybutadiene is used as the oxidizing organic component, further, it is desired to add the oxidizing organic component at a ratio of 0.1 to 10% by weight from the standpoint of obtaining the above-mentioned particle size and the particle size profile.

[0042]

The packing body of the invention having the above-

mentioned islands-in-the-sea structure may be blended with various blending agents such as filler, coloring agent, heat stabilizer, weather stabilizer, antioxidant, age resistor, photo stabilizer, ultraviolet ray absorber, antistatic agent, lubricant such as metal soap or wax, reforming resin or rubber in a range in which they do not spoil the islands-in-the-sea structure or the moldability. [0043]

The packing body of the invention can be realized as a single-layer packing body comprising a layer having the above-mentioned phase structure making it possible to express oxygen absorbing gas barrier property in an early time. Further, since the layer having oxygen absorbing barrier property has a thickness larger than that of the multi-layer structure having other resin layers as inner and outer layers, the amount of the oxygen absorbing gas barrier resin composition is large and the function such as gas barrier property can be sustained for extended periods of time. Besides, since no interlayer peeling occurs, excellent strength is obtained which is an advantage. Though there is no particular limitation on the thickness of the single-layer packing body, the thickness is, usually, in a range of 10 to 1000  $\mu\text{m}$  and, particularly, 100 to 500  $\mu\text{m}$ .

Though the packing body of the invention is desirably the single-layer packing body as described above, it is also allowable to provide other layers as required.

[0044]

[Use]

The plastic packing body of the invention can assume the form of an intermediate molded article such as film, sheet, bottle or parison or pipe for forming tubes, or preform for forming bottles or tubes. Through the intermediate molded article, the plastic packing body of the invention is finally used as a cup, a tray, a bottle, a tubular container, a pouch or a container lid.

[0045]

By using, for example, an extruder or an injection

machine, the composition is extrusion-molded or injection-molded in a known manner and, as required, is compression-molded to form an intermediate molded article.

The film which is an intermediate molded article is, as required, biaxially stretched and is used as a biaxially stretched film.

The bottle can be easily molded from a parison, a pipe or a preform by pinching off the extruded article by a pair of split molds, and flowing a fluid therein.

Further, the pipe or the preform after cooled is heated at a stretching temperature, stretched in the axial direction, and is blow-stretched in the circumferential direction by utilizing a fluid pressure to obtain a stretch-blown bottle.

Moreover, the film or the sheet is subjected to the vacuum molding, compressed-air molding, expansion molding or plug-assisted molding to obtain a packing body of the shape of a cup or a tray or a container lid.

Further, the film can be used as a packing bag (pouch) in a variety of forms, and the bags can be produced according to a known method.

[0046]

The plastic packing body of the invention is very useful, particularly, as a container for preventing a drop of taste of the content due to oxygen.

For example, the plastic packing body of the invention can be applied to the containers for containing beverages such as beer, wine, fruits juice, carbonated soft drinks, etc., as well as fruits, nuts, vegetables, meats, infant's foods, coffee, jam, mayonnaise, ketchup, edible oils, dressings, sauces, food boiled down in soy, milk products, medicines, cosmetics, gasoline and the like, that are liable to be deteriorated by the presence of oxygen.

Further, the plastic packing body of the invention has excellent transparency and can be favorably used as a packing body that requires transparency.

[0047]

[EXAMPLES]



The present invention will now be further described by way of the following examples, which, however, are not to limit the invention.

[0048]

1. [Measuring the melt viscosities]

By using a capillograph (manufactured by Toyo Seiki Co.), melt viscosities of the oxygen absorbing gas barrier resin composition and of the polyethylene terephthalate were measured with capillary L/D = 10/1 (mm) and at a cylinder temperature of 270°C. A melt viscosity ratio ( $\eta_{(\text{barrier})} / \eta_{(\text{PET})}$ ) at a strain rate of 182 sec<sup>-1</sup> was calculated from a curve of the obtained melt viscosities.

[0049]

2. [Measuring the average domain diameter and the number of domains]

A sample piece 2 mm wide and 30 mm long was cut out from the preform, was surfaced in cross section thereof by using an ultramicrotome, and was put to the pretreatment, i.e., platinum was vapor-deposited in vacuum at 10 mA for 60 seconds. The sectional surface of the pretreated test piece was observed by using a scanning type electron microscope (JMS-6300F: manufactured by Nihon Denshi Co.) at an acceleration voltage of 3 kV, was photographed at a magnification of 3000 times, and the total number of the domains in the photograph was counted. By giving attention to the island portions, further, the longest diameters and the shortest diameters of the domains were measured, and an average domain diameter and a parameter Q representing the width of distribution of the domain diameters were found from the formulas (1) and (2).

[0050]

5. [Measuring the haze]

A sample piece 40 mm wide and 30 mm long was cut out from the shoulder portion of a bottle. The sample piece was measured for its haze (%) by using the S & M COLOUR COMPUTER MODEL SM-4 (manufactured by Suga Shikenki Co.).

[0051]

4. [Measurement of concentration of oxygen dissolved in water in the bottle]

Oxygen-free water was obtained by using an oxygen-free water-producing device (LOW DISSOLVED OXYGEN: manufactured by Miura Kogyo Co.). The single-layer bottle that has been prepared was fully filled with the oxygen-free water while flowing a nitrogen gas in a manner that the air bubbles were not mixed, and was sealed with an aluminum cap. The bottle was preserved in a constant-temperature constant-humidity chamber maintained at 22°C 60%RH for 80 days. The concentration of oxygen dissolved in water in the bottles was measured by using an instrument for measuring the concentration of oxygen dissolved in water (oxygen indicator: Orbisphere Laboratories).

[0052]

[Example 1]

By using a polymetaxylyleneadipamide (MXD6) resin (T600: manufactured by Toyo Boseki Co.) as the gas barrier resin, an oxygen absorbing gas barrier resin composition was prepared using a biaxial extruder and was pelletized, the oxygen absorbing gas barrier resin composition containing 5% by weight of a maleic acid-modified polybutadiene (M2000-20: manufactured by Nihon Sekiyu Kagaku Co.) as the oxidizing organic component and 350 ppm, calculated as cobalt, of cobalt neodecanoate (DICNATE 5000: manufactured by Dainihon Ink Kagaku Kogyo Co.) as the transition metal catalyst. A dry blend of the pellets of the polyethylene terephthalate (PET) resin (RT543CTHP: manufactured by Nihon Unipet Co.) as the polyester resin and the above resin composition at a weight ratio of 50:50, was molded into a preform by using an injection molding machine. The cross section of the preform was observed by using an electron microscope, and the average domain diameter and the parameter Q were found. Further, the above preform was biaxially stretch-blow-molded to prepare a single-layer bottle, and the haze of the shoulder portion thereof was measured. By using the obtained bottle, further, the oxygen-free water testing was conducted.

[0053]

## [Example 2]

A preform was molded and the phase structure was analyzed in the same manner as in Example 1 but dry-blending the oxygen absorbing gas barrier resin composition and the polyester resin at a weight ratio of 30:70. Further, the biaxially stretch-blow-molded bottle was measured for its haze at the shoulder portion and was subjected to the oxygen-free water testing.

[0054]

## [Example 3]

A preform was molded and the phase structure was analyzed in the same manner as in Example 1 but mixing the oxygen absorbing gas barrier resin composition and a PET resin having a low melt viscosity (NES2040: manufactured by Unitika Co.) at a weight ratio of 70:30. Further, the biaxially stretch-blow-molded bottle was measured for its haze at the shoulder portion and was subjected to the oxygen-free water testing.

[0055]

## [Example 4]

A preform was molded and the phase structure was analyzed in the same manner as in Example 3 but mixing the oxygen absorbing gas barrier resin composition and the PET resin at a weight ratio of 50:50. Further, the biaxially stretch-blow-molded bottle was measured for its haze at the shoulder portion and was subjected to the oxygen-free water testing.

[0056]

## [Example 5]

A preform was molded and the phase structure was analyzed in the same manner as in Example 1 but using an oxygen absorbing gas barrier resin composition obtained in the same manner as in Example 1 but using the MXD 6 resin having a high melt viscosity (T660: manufactured by Toyobo Co.) as the gas barrier resin, mixing the oxygen absorbing gas barrier resin composition with the polyester resin at a weight ratio of 50:50, pelletizing the mixture again and injection-molding the mixture. Further, the biaxially stretch-blow-molded bottle was measured for its haze at

the shoulder portion and was subjected to the oxygen-free water testing.

[0057]

[Comparative Example 1]

A preform was molded in the same manner as in Example 1 but dry-blending the oxygen absorbing gas barrier resin composition and the polyester resin at a weight ratio of 90:10. Further, the biaxially stretch-blow-molded bottle thereof was subjected to the oxygen-free water testing.

[0058]

[Comparative Example 2]

A preform was molded in the same manner as in Example 1 but dry-blending the oxygen absorbing gas barrier resin composition and the polyester resin at a weight ratio of 80:20. Further, the biaxially stretch-blow-molded bottle thereof was subjected to the oxygen-free water testing.

[0059]

[Comparative Example 3]

47.5% by weight of the MXD 6 (T600: manufactured by Toyobo Co.) as the gas barrier resin, 2.5% by weight of a maleic acid-modified polybutadiene (M2000-20: manufactured by Nihon Seikiyu Kagaku Co.) as the oxidizing organic component, 50% by weight of a PET resin having a low melt viscosity (NES 2040: manufactured by Unitika Co.) as the polyester resin, and a cobalt neodecanoate (DECNATE 5000: manufactured by Dainihon Ink Kagaku Kogyo Co.) as the metal catalyst in an amount of 350 ppm calculated as cobalt with respect to the gas barrier resin, were melted, kneaded and pelletized by using the biaxial extruder and was molded into a preform by using an injection-molding machine. The obtained preform was biaxially stretch-blow-molded into a single-layer bottle which was measured for its haze at the shoulder portion thereof.

[0060]

[Comparative Example 4]

A preform was molded and the phase structure was analyzed in the same manner as in Example 1 but using the

MXD 6 (T600: manufactured by Toyobo Co.) having a high melt viscosity as the gas barrier resin, and dry-blending the oxygen absorbing gas barrier resin composition and the polyester resin at a weight ratio of 60:40. Further, the biaxially stretch-blow-molded bottle thereof was measured for its haze at the shoulder portion thereof and was subjected to the oxygen-free water testing.

[0061]

[Comparative Example 5]

A preform was molded and the phase structure was analyzed in the same manner as in Comparative Example 4 but mixing the oxygen absorbing gas barrier resin composition and the polyester resin at a weight ratio of 50:50. Further, the biaxially stretch-blow-molded bottle thereof was measured for its haze at the shoulder portion and was subjected to the oxygen-free water testing.

Table 1

|           | Polyester resin (wt.%) | Oxygen absorbing gas barrier resin |                                   |                                 | Melt viscosity ratio $\eta$ (barrier)/ $\eta$ (PET) | Blending method  |
|-----------|------------------------|------------------------------------|-----------------------------------|---------------------------------|---|--|
|           |                        | Polyamide resin (wt%)              | Oxidizing organic component (wt%) | Transition metal catalyst (ppm) |   |  |
| Ex.1      | 50                     | 47.5                               | 2.5                               | 350                             | 0.82  | MXD6, Ma-pbd, Co were biaxially kneaded and dry-blended with PET                 |
| Ex.2      | 70                     | 28.5                               | 1.5                               | 350                             | 0.82  | ditto  |
| Ex.3      | 30                     | 66.5                               | 3.5                               | 350                             | 1.28  | ditto  |
| Ex.4      | 50                     | 47.5                               | 2.5                               | 350                             | 1.28  | ditto  |
| Ex.5      | 50                     | 47.5                               | 2.5                               | 350                             | 2.02  | MXD6, Ma-pbd, Co were biaxially kneaded and, further, biaxially kneaded with PET |
| Comp.Ex.1 | 10                     | 85.5                               | 4.5                               | 350                             | 0.82  | MXD6, Ma-pbd, Co were biaxially kneaded and dry-blended with PET                 |
| Comp.Ex.2 | 20                     | 76                                 | 4                                 | 350                             | 0.82  | ditto  |
| Comp.Ex.3 | 50                     | 47.5                               | 2.5                               | 350                             | ----  | MXD6, Ma-pbd, Co, PET were biaxially kneaded                                     |
| Comp.Ex.4 | 40                     | 57                                 | 3                                 | 350                             | 2.02  | MXD6, Ma-pbd, Co were biaxially kneaded and dry-blended with PET                 |
| Comp.Ex.5 | 50                     | 47.5                               | 2.5                               | 350                             | 2.02  | ditto  |

Table 1 (continued)

| Sea Component | Island component               | Ave. domain diameter of islands (μm) | Dispersion parameter Q | HAZE (%) | Dissolved oxygen concentration (22°C, 80 days) (ppb)         |     |
|---------------|--------------------------------|--------------------------------------|------------------------|----------|--|-----|
|               |                                |                                      |                        |          |  |     |
| Ex. 1         | PET/Co                         | MXD6/MA-Pbd/Co                       | 3.19                   | 0.71     | 18.4   | 93  |
| Ex. 2         | PET/Co                         | MXD6/MA-Pbd/Co                       | 1.33                   | 0.85     | 10.9   | 77  |
| Ex. 3         | PET/Co                         | MXD6/MA-Pbd/Co                       | 2.83                   | 0.81     | 16.4   | 110 |
| Ex. 4         | PET/Co                         | MXD6/MA-Pbd/Co                       | 1.48                   | 0.79     | 15.2   | 85  |
| Ex. 5         | PET/Co                         | MXD6/MA-Pbd/Co                       | 1.86                   | 0.69     | 14.4   | 103 |
| Comp.Ex.1     | ----- island component was PET | -----                                |                        |          | Preform absorbed moisture, and bottle was defectively molded |     |
| Comp.Ex.2     | ----- island component was PET | -----                                |                        |          | ditto  |     |
| Comp.Ex. 3    | PET/Ma-pbd/Co                  | MXD6/MA-Pbd/Co                       | --                     | --       | 72.3   | --  |
| Comp.Ex. 4    | PET/Co                         | MXD6/MA-Pbd/Co                       | 4.3                    | 0.58     | 31.2   | 124 |
| Comp.Ex. 5    | PET/Co                         | MXD6/MA-Pbd/Co                       | 1.58                   | 0.67     | 22.2   | 92  |

\*Ma-pbd: maleic anhydride-modified polybutadiene

[0063]

[Effects of the Invention]

The plastic packing body of the invention has an islands-in-the-sea structure constituted by a sea portion of a polyester resin and island portions of an oxygen absorbing gas barrier resin composition containing an oxidizing organic component and a transition metal catalyst, wherein no oxidizing organic component is present in the sea portion. Therefore, the plastic packing body features excellent functions such as gas barrier property due to the oxygen absorbing gas barrier resin composition, and exhibits excellent transparency.

[Brief Description of the Drawings]

[Fig. 1] is a view schematically illustrating an electron microphotograph of a sheet comprising a dry blend of a polyester resin and an oxygen absorbing gas barrier resin composition.

[Fig. 2] is a view schematically illustrating an electron microphotograph of a sheet comprising a blend of four components of a polyester resin, a polyamide resin, an oxidizing organic component and a transition metal catalyst.

[Fig. 3] is a diagram showing hazes of sheets of Fig. 1 and Fig. 2 that are longitudinally and transversely stretched into 3 times x 3 times.

[Fig. 4] is a diagram showing a relationship between the dispersion parameter  $Q$  and the haze.



Fig. 1

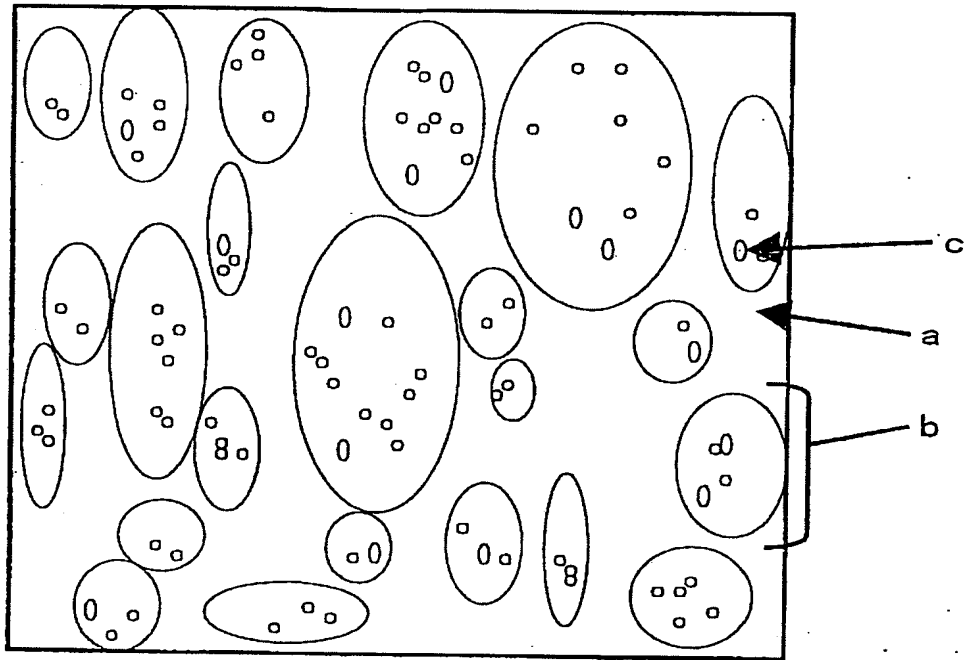


Fig. 2

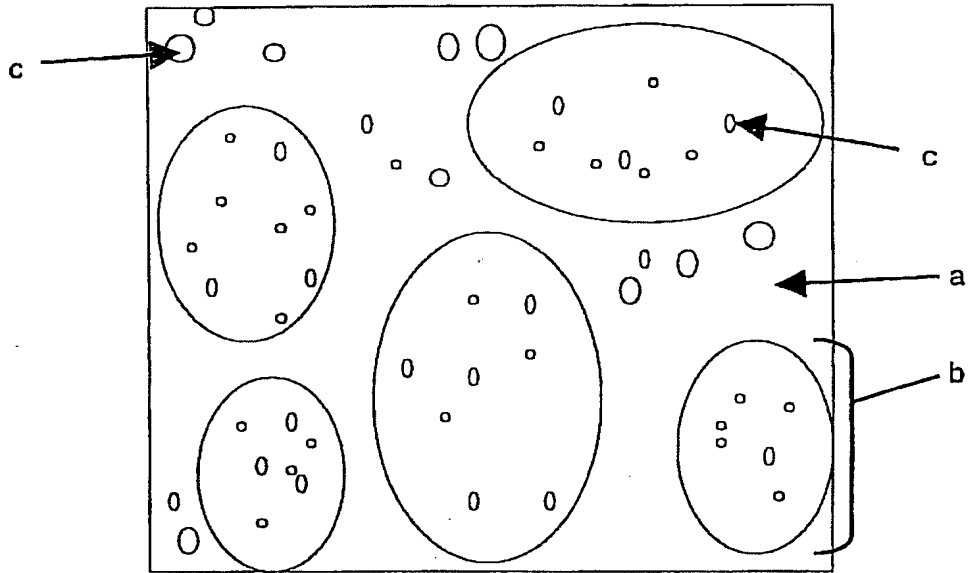
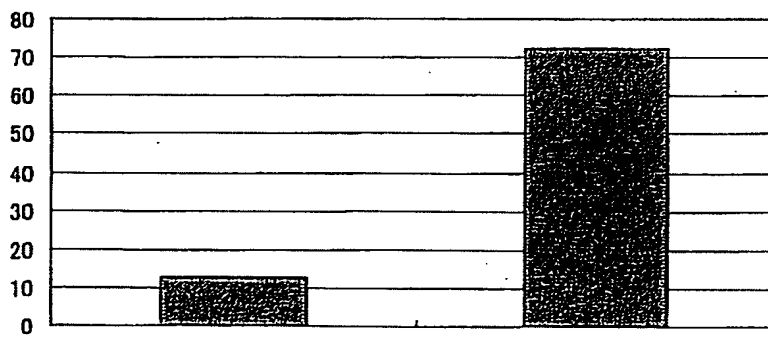


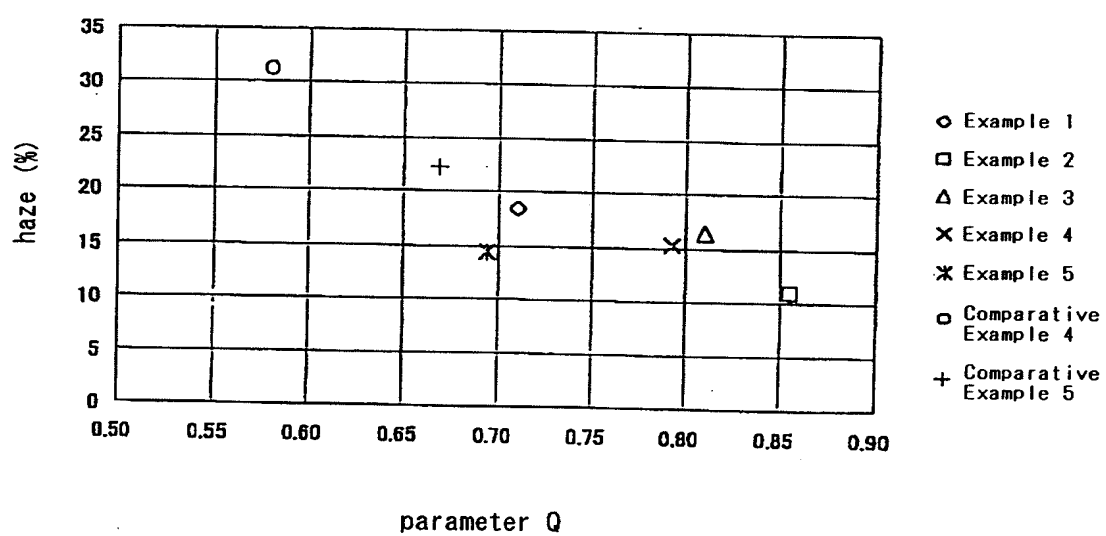
Fig. 3



Sheet of Fig. 1

Sheet of Fig. 2

Fig. 4



[Designation of Document] Abstract

[Abstract]

[Problems] To provide a plastic packing body capable of efficiently exhibiting such functions as gas barrier property and having excellent transparency and, particularly, initial oxygen absorbing barrier property.

[Means for Solution]

A plastic packing body having an islands-in-the-sea structure constituted by a sea portion of a polyester resin and island portions of an oxygen absorbing gas barrier resin composition containing an oxidizing organic component and a transition metal catalyst, wherein no oxidizing organic component is present in the sea portion. The plastic packing body features excellent functions such as gas barrier property due to the oxygen absorbing gas barrier resin composition, and exhibits excellent transparency.

[Selected Drawing] Fig. 5